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## (54) SOLID NITROGENOUS POLYELECTROLYTE

### (57)Abstract:

PURPOSE: To obtain the title electrolyte comprising a polymer support and a supporting electrolyte and excellent in ionic conductivity, film-forming property, processability, flexibility, adherence to an electrode, etc., by using a specific polymer as the support.

CONSTITUTION: The polyelectrolyte comprises a polymer support and a supporting electrolyte, which is a crosslinked comb polymer obtained by crosslinking a comb polymer comprising a poly(ethylene imine), as the main chain, represented by the formula -(NH-CH<sub>2</sub>CH<sub>2</sub>)<sub>1</sub>- wherein 1 is 3 to 1×10<sup>7</sup> and one or more side chains each bonded to a nitrogen atom of the main chain and represented by the formula X-O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>R<sub>1</sub> wherein X is a group represented by the formula O=C=N-R<sub>2</sub>-NH-CO-where R<sub>2</sub> is an arylene or alkylene; R<sub>1</sub> is a lower alkyl; and m is 3-100, the number of the side chains being at least 5% of the number of all nitrogen atoms of the main chain. The crosslinking is conducted with a crosslinking agent represented by the formula X-O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>-X wherein n is 3-200 to such a degree that 1-95% of the nitrogen atoms of the main chain each has the crosslinked side chain.

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CLAIMS

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[Claim(s)]

[Claim 1] It sets to the solid polymer electrolyte which consists of a macromolecule base material and a supporting electrolyte, and a macromolecule base material is a formula (1).

- The inside l of a NH-CH<sub>2</sub> CH<sub>2</sub> l-[type is the formula (2) permuted at least by the N of the polyethyleneimine principal chain shown by] which shows the integer of three to 1x10<sup>7</sup>, and this principal chain.

The inside X of a X-O-(CH<sub>2</sub> CH<sub>2</sub> O) m-R1[type the piece end reactant of diisocyanate shown by O=C=N-R<sub>2</sub>-NH-CO-(R<sub>2</sub> is an arylene chain or an alkylene chain) R1 It is a formula (3) about the Kushigata macromolecule whose rate of addition of a side chain [ as opposed to / m consists a low-grade alkyl group of a polyethylene oxide system side chain shown by] which shows the integer of 3-100, respectively, and / the nitrogen atom of the above-mentioned principal chain ] is at least 5%.

It is the nitrogen-containing solid polymer electrolyte characterized by being the bridge formation Kushigata macromolecule whose rate of bridge formation of the side chain to the nitrogen atom of the above-mentioned principal chain which is made to construct a bridge by the polyethylene oxide system cross linking agent shown by X-O-(CH<sub>2</sub> CH<sub>2</sub>-O) n-X [it is the same as the above the inside X of a formula, and n shows the integer of 3-200], and is obtained is 1 - 95%.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a nitrogen-containing solid polymer electrolyte and the more detailed above-mentioned solid electrolyte useful for electrochemistry components, such as a cell, an electrochromic display device, an electroluminescence display device, a capacitor, and a sensor, etc.

[0002]

[Description of the Prior Art] Since the electrolytic solution is being used for electrochemistry components, such as a cell, an electrochromic device, and a capacitor, there is a problem in the fall of the dependability by the liquid spill, workability, productivity, etc., and researches and developments of a solid electrolyte without problems, such as this, have been activating them in recent years. Also in this solid electrolyte, since a solid polymer electrolyte is lightweight compared with an inorganic system solid electrolyte, it has flexibility, it excels in shaping, workability, etc. and it excels also in adhesion with an electrode, attention is attracted.

[0003] According to use of the macromolecule base material which made the side chain carry out the graft of the low-molecular polyethylene oxide (PEO) to a principal chain previously using the Polyethylenimine (PEI) which takes regular higher order structure and has a high polarity as a result of this invention persons' also taking lessons from the above-mentioned polyelectrolyte and piling up research wholeheartedly, while having high ionic conductivity, it found out that the solid polymer electrolyte in which the film cast is possible was obtained, and patent application of the invention concerning this knowledge was carried out (refer to JP,4-270762,A).

[0004] However, when the suitable polar solvent was made to mix as a plasticizer, or when a temperature up was carried out to about 70 degrees C, the solid polymer electrolyte concerning application of an above place had the fault which liquefies and by which dimensional stability is spoiled, in order to raise ionic conductivity further.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the new solid polymer electrolyte which cancels entirely the fault looked at by the above-mentioned conventional solid polymer electrolyte and the macromolecule base material especially used for this, and has high ionic conductivity, good membrane formation workability, flexibility, good adhesion with an electrode, etc. and which is demanded in the field.

[0006]

[Means for Solving the Problem] When using the giant molecule over which the Kushigata giant molecule which consists of a Polyethylenimine principal chain of the following specification and a polyethylene RENEKI side system side chain as a giant-molecule base material was made to construct a bridge by the predetermined polyethylene oxide system cross linking agent as a result of repeating research further succeedingly from the above-mentioned purpose, this invention person finds out that the solid polymer electrolyte corresponding to the above-mentioned purpose is obtained, and came to complete this invention here.

[0007] That is, it sets to the solid polymer electrolyte which consists of a macromolecule base material and a supporting electrolyte according to this invention, and a macromolecule base material is a formula (1).

- The inside l of a NH-CH<sub>2</sub> CH<sub>2</sub> l-[type is the formula (2) permuted at least by the N of the polyethylenimine principal chain shown by] which shows 3-1x107 integer, and this principal chain.

The inside X of a X-O-(CH<sub>2</sub> CH<sub>2</sub> O) m-R1[type the piece end reactant of diisocyanate shown by O=C=N-R<sub>2</sub>-NH-CO-(R<sub>2</sub> is an arylene chain or an alkylene chain) R1 It is a formula (3) about the Kushigata macromolecule whose rate of addition of a side chain [ as opposed to / m consists a low-grade alkyl group of a polyethylene RENEKI side system side chain shown by] which shows the integer of 3-100, respectively, and / the nitrogen atom of the above-mentioned principal chain ] is at least 5%.

The nitrogen-containing solid polymer electrolyte characterized by being the bridge formation Kushigata macromolecule whose rate of bridge formation of the side chain to the nitrogen atom of the above-mentioned principal chain which is made to construct a bridge by the polyethylene oxide system cross linking agent shown by X-O-(CH<sub>2</sub>

$\text{CH}_2\text{-O}$ ) $n$ -X [it is the same as the above the inside X of a formula, and n shows the integer of 3-200], and is obtained is 1 - 95% is offered.

[0008] If it explains in full detail hereafter per [ which is used in this invention solid polymer electrolyte ] macromolecule base material, this macromolecule base material will use the polyethyleneimine (PEI) principal chain shown by said formula (1) as a principal chain which constitutes this. The polyethyleneimine compounded for example, from 2-oxazoline as the example can be used [Macromolecules Communications to Editor, 5, and for example, refer to 108 (1972)]. As for this principal chain, it is desirable to have about 15 to 50 chain length (l in a formula (1)) generally.

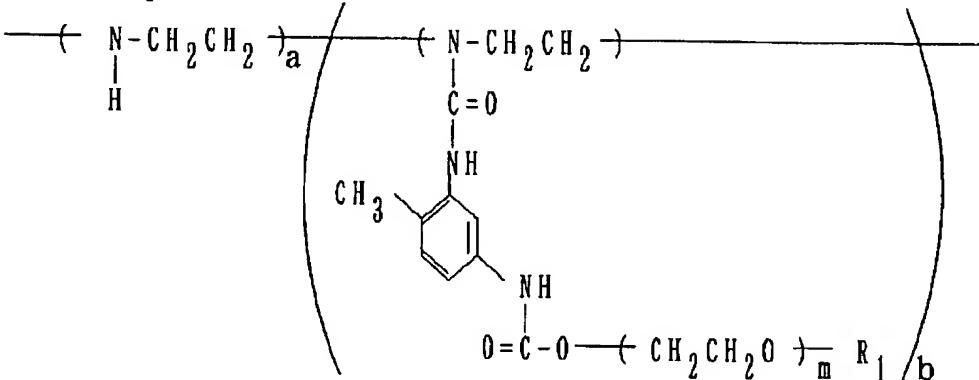
[0009] this invention base material consists of side chains permuted at least by the N of the above-mentioned PEI principal chain and this principal chain, and this side chain consists of derivatives of the polyethylene oxide (PEO) shown by said formula (2) introduced in the JIISO cyanic-acid derivative which functions as a polar dissociable group. As for installation of this PEO system side chain, for example, a piece end is protected by the low-grade alkyl group (R1). The PEO derivative whose piece end of another side is a hydroxyl group, for example, the trimer of ethylene glycol monomethyl ether, 100 \*\*\*\*\*, etc. in aprotic solvents, such as dimethyl sulfoxide (DMSO) JIISO cyanic-acid derivatives, such as 2 and 4-JIISO cyanic-acid tolylene, and the PEO system derivative shown by said formula (2) which corresponds by making it react with 1:1-mol equivalence are compounded, and it can carry out by subsequently making this react with the shape of a straight chain PEI corresponding to said PEI principal chain. Here, as a low-grade alkyl group, methyl, ethyl, propyl, isopropyl, butyl, etc. can be illustrated, for example. moreover -- as a JIISO cyanic-acid derivative -- R2 \*\*\*\*\* -- each of various kinds of derivatives which has the shape of a straight chain and annular alkylene chains, such as arylene chains, such as tolylene, a xylene, and a meta-xylene, hexamethylene, trimethylhexamethylene, and an isophorone, can be used. Although especially the reaction condition of each above-mentioned reaction is not limited, a PEO system derivative composition reaction is carried out by generally mixing a raw material under about [ room temperature -80 degree C ] temperature, and in an inert gas ambient atmosphere and an aprotic solvent, and the introductory reaction of a side chain is usually carried out by usually mixing a raw material under the temperature of about 100-160 degrees C, and in an inert gas ambient atmosphere and an aprotic solvent. Moreover, the PEO system derivative for introducing a side chain is the rate which becomes five to about 500 to the unit unit 100 of the principal chain of the macromolecule base material usually obtained, it is desirable to be used to the shape of a straight chain PEI, and the PEI principal chain-PEO system side-chain macromolecule of the request whose rate of addition of the side chain to the nitrogen atom of a principal chain is at least 5% can be acquired in this way. When there are too few operating rates of a PEO system derivative than the above 5, the rate of installation of a side chain falls and there is a fault to which the ionic conductivity of the macromolecule obtained falls. Conversely, when exceeding the above 500, there is disadvantage which unreacted objects increase in number too much, and the removal takes complicated actuation.

[0010] In addition, if independent, it is a liquid, but in this invention base material, since [ its ] this exists as a side chain, the low-molecular-weight object like the PEO system derivative shown by the above-mentioned formula (2) can expect that micro Brownian motion of the PEO chain which is excellent in dimensional stability and is greatly contributed to conduction of ion will be performed actively.

[0011] The PEI principal chain-PEO system side-chain giant molecule obtained in this way has the \*\*\*\* Kushigata structure shown by the following formula (4), if the case where 2 and 4-JIISO cyanic-acid tolylene is used is taken for an example.

[0012]

[Formula 1]



[0013] inside R1 of a formula and m -- the above -- the same -- it is  $a+b=1$  and  $95>100 b/a+b>5$  are shown.

[0014] this invention base material is manufactured by carrying out crosslinking reaction of the above-mentioned PEI principal chain-PEO system side-chain Kushigata giant molecule using the polyethylene oxide (PEO) system cross

linking agent shown by said formula (3). This PEO system cross linking agent is obtained by making PEO (n=3-200) whose both ends are hydroxyl groups react in aprotic solvents, such as DMSO, with 2 double mol equivalence of JIISO cyanic-acid derivatives, such as 2 and 4-JIISO cyanic-acid tolylene. This reaction can be carried out under the same reaction condition as said PEO system derivative composition reaction and abbreviation. Moreover, crosslinking reaction of the PEI principal chain-PEO system side-chain Kushigata macromolecule using this cross linking agent can be carried out under the same reaction condition as the introductory reaction of said side chain, and abbreviation, and, as for the addition of a PEO system cross linking agent, it is desirable to be chosen so that the rate of bridge formation may become about 5 - 60%. The rate of bridge formation is shown by the use mole ratio (percentage) of the cross linking agent to the nitrogen atom of a principal chain here. There is an inclination for the mechanical strength and dimensional stability of the macromolecule obtained to fall when this rate of bridge formation does not fall the above-mentioned range (i.e., when there are too few operating rates of the PEO system cross linking agent to a PEI principal chain-PEO system side-chain macromolecule), when there are too many operating rates of a cross linking agent conversely, the ionic conductivity of a macromolecule tends to fall and neither is desirable.

[0015] Of the crosslinking reaction which used the above-mentioned PEO system cross linking agent in this way, a desired bridge formation Kushigata macromolecule base material is formed for this cross linking agent in response to the unreacted NH radical which exists in the PEI principal chain of said PEI principal chain-PEO system side-chain Kushigata macromolecule.

[0016] The above-mentioned macromolecule base material can be used as the self-standing nitrogen-containing solid polymer electrolyte of the request which has high ionic conductivity and the membrane formation nature which was excellent with addition of an elevated temperature or a plasticizer by infiltrating a supporting electrolyte into this according to a conventional method.

[0017] Especially the supporting electrolyte used here may not be restricted and any of various kinds of well-known things are sufficient as it, as the example -- various kinds, such as inorganic acids, such as organic acids, such as p-toluenesulfonic acid, an acetic acid, oxalic acid, a polyvinyl sulfonic acid, trifluoro methansulfonic acid, and trifluoroacetic acid, a phosphoric acid, perchloric acid, thiocyanic acid, a tetra-chloro boric acid, hexa fluorophosphoric acid, trifluoroacetic acid, and a nitric acid, -- various kinds of salts by the reaction with the 4th class ammonium, such as various acids, such as acids and this, a halogen and alkali metal, an alkaline earth metal, tetrabutylammonium, and tetraethylammonium, etc. can be illustrated. According to the usual approach, it can perform also sinking [ of supporting electrolytes, such as this ] in. More specifically said macromolecule base material and supporting electrolyte are dissolved in mixed solvents, such as solvents, such as an acetonitrile, chloroform, a methanol, N.N-dimethylformamide, dimethyl sulfoxide, propylene carbonate, ethylene carbonate, and diethyl carbonate, and this, the approach of carrying out the film cast of the solution obtained, and said macromolecule base material and supporting electrolyte are mixed to homogeneity with a non-solvent, and the approach of dissolving a supporting electrolyte at the temperature which a macromolecule base material softens etc. can be illustrated.

[0018] this invention nitrogen-containing solid polymer electrolyte obtained in this way shows ionic conductivity (sigma) with usually high about 1x10<sup>-3</sup> - 1x10<sup>-8</sup> S/cm extent.

[0019]

[Effect of the Invention] this invention nitrogen-containing solid polymer electrolyte is effective as an electrolyte which has ionic conductivity (sigma) with usually high about 1x10<sup>-3</sup> - 1x10<sup>-8</sup> S/cm extent, has flexibility, and excelled for electrochemistry components, such as a cell, a capacitor, an electrochromic display device, and a sensor. Especially the solid electrolyte of this invention has the very high ionic conductivity in ordinary temperature, and is very effective in manufacture of the cell which was excellent in the charge-and-discharge property, a capacitor, an electrochromic display device with an early speed of response, an electroluminescence display device with high luminous efficiency, a sensor, etc.

[0020]

[Example] Hereafter, in order to explain this invention in more detail, an example and the example of a comparison are given.

[0021]

[Example 1] Aldrich (Aldrich) The living polymerization object of shrine 2-methyl-2-oxazoline was hydrolyzed as follows, and the PEI principal chain was compounded [refer to [ Macromolecules, 8, and ] 390 (1975)]. The preparation mole ratio could be 1/30, using p-toluenesulfonic-acid methyl as a living polymerization initiator of 2-methyl-2-oxazoline. The reaction flowed back in the inert gas ambient atmosphere by having used the acetonitrile as the solvent, and the gas chromatography determined termination of a reaction.

[0022] Pori (N-acetyl imine) of 30 \*\*\*\* obtained in this way was used as the water solution of about 100 g/l equivalence, NaOH of about 900 g/l equivalence was further added to this, it flowed back one whole day and night, and the straight chain-like polyethyleneimine (PEI, 30 \*\*\*\*) corresponding to a principal chain was obtained.

[0023] As a PEO derivative corresponding to a side chain, he is Aldrich (Aldrich). Shrine Pori (ethylene glycol methyl ether) (average-molecular-weight =550, average degree of polymerization = 12.8) was used.

[0024] Addition of the PEO derivative to Above PEI was performed using 2 and 4-JIISO cyanic-acid tolylene as follows. That is, Pori (ethylene glycol methyl ether) was mixed by the mole ratio of 1:1 in inert gas to 2 and 4-JIISO cyanic-acid tolylene among the dimethyl sulfoxide solvent, it agitated at the room temperature one whole day and night, and the PEO system derivative which can form the side chain corresponding to said formula (2) first was compounded.

[0025] In order to remove unreacted 2 and 4-JIISO cyanic-acid tolylene from the obtained reaction mixed solution, vacuum distillation was performed, PEI (the amount of equivalent units) subsequently to this compounded by dimethyl sulfoxide and the above was added one by one, and the dimethyl sulfoxide solution containing the Kushigata giant molecule which agitates one whole day and night and consists of a PEI principal chain-PEO system side chain was obtained.

[0026] The rate of addition of the side chain of the macromolecule obtained above was proved from the result of elemental analysis that it is 64%.

[0027] As a PEO system cross linking agent, he is Aldrich (Aldrich). Shrine Pori (ethylene glycol) (average-molecular-weight =1500, average degree of polymerization = 33.7) was used.

[0028] The above-mentioned PEO system cross linking agent was made to add to said Kushigata macromolecule. That is, the cross linking agent which carries out 1/2-mol equivalent mixing of Pori (ethylene glycol) in inert gas among a dimethyl sulfoxide solvent at 2 and 4-JIISO cyanic-acid tolylene, agitates at a room temperature one whole day and night, and is shown by said formula (3) was obtained.

[0029] In order to remove unreacted 2 and 4-JIISO cyanic-acid tolylene from the obtained reaction mixed solution, vacuum distillation was performed, the Kushigata giant molecule subsequently to this compounded by dimethyl sulfoxide and the above was added one by one, it flowed back one whole day and night, and the dimethyl sulfoxide solution containing the target bridge formation Kushigata giant molecule was obtained.

[0030] Vacuum distillation of the obtained solution was carried out, after having removed the JIMETORU sulfoxide from the reaction mixture, dissolving the residue in the acetonitrile after that and making it reprecipitate by diethylether, similarly, the methanol and the benzene solution were made to reprecipitate by diethylether, and separation purification of the target macromolecule base material was carried out.

[0031] The rate of bridge formation of the obtained macromolecule base material was proved from the elemental-analysis result that it is 28%.

[0032] After drying this macromolecule base material and making it a heat (DMSO+PC (1:1)) solution, solvent exchange was performed to the acetonitrile, after dissolving the lithium perchlorate which becomes 10.2 % of the weight to a macromolecule base material, after having carried out the film cast, drying at the room temperature one whole day and night and removing a solvent with air, the vacuum drying was carried out at 130 degrees C, and the solid polymer electrolyte was prepared for further 10 hours.

[0033] Glass transition temperature and ionic conductivity ( $\sigma$ ) were measured as physical properties of the obtained solid polymer electrolyte.

[0034] The glass transition temperature measured by DSC by SEIKO electronic industry incorporated company 220C was -48.7 degrees C.

[0035] Solar TRON (Solartron) Shrine 1260 The temperature dependence of the ionic conductivity ( $\sigma$ ) evaluated by measuring an alternating current impedance in 1Hz - 10MHz, and obtaining Cole-ColePlot by IMPEDANCE/GAIN-PHASE ANALYZER was as being shown in the following table 1.

[0036]

[Table 1]

温 度 (°C)	$1000/T$ ( $10^{-3} \cdot K^{-1}$ )	$\sigma$ (S/cm)	Log [ $\sigma$ (S/cm)]
86.0	2.78	$2.0 \times 10^{-3}$	-2.7
78.4	2.84	$1.6 \times 10^{-3}$	-2.8
72.7	2.89	$1.4 \times 10^{-3}$	-2.8
66.3	2.95	$1.2 \times 10^{-3}$	-2.9
61.2	2.99	$1.1 \times 10^{-3}$	-3.0
51.9	3.08	$7.6 \times 10^{-4}$	-3.1
46.0	3.13	$6.2 \times 10^{-4}$	-3.2
39.2	3.20	$4.5 \times 10^{-4}$	-3.3
35.0	3.25	$3.8 \times 10^{-4}$	-3.4
30.2	3.30	$3.0 \times 10^{-4}$	-3.5
25.8	3.35	$2.4 \times 10^{-4}$	-3.6
21.9	3.39	$1.9 \times 10^{-4}$	-3.7
15.8	3.46	$1.4 \times 10^{-4}$	-3.9
-0.3	3.67	$4.0 \times 10^{-5}$	-4.4
-2.9	3.70	$3.2 \times 10^{-5}$	-4.5
-8.2	3.77	$1.8 \times 10^{-5}$	-4.7

[0037] this invention solid polymer electrolyte film shows high ionic conductivity called  $2 \times 10^{-4}$  S/cm at a room temperature, and the temperature dependence is also still lower, for example, it is clearer than this table that its at least -8 degrees C of outstanding properties of  $2 \times 10^{-5}$  S/cm are shown.

[0038]

[Example 2] Although the bridge formation Kushigata macromolecule base material for this invention solid polymer electrolyte was prepared in the example 1 by carrying out the sequential addition reaction of a side chain and the cross linking agent, in this example, the addition reaction of both was carried out by the mixed state, and the base material for a desired solid polymer electrolyte was prepared.

[0039] That is, he is Aldrich (Aldrich) as a PEO derivative for side chains. It is shrine Pori (ethylene glycol methyl ether) (average-molecular-weight = 550, average degree of polymerization = 12.8) as a PEO derivative for cross linking agents. Aldrich (Aldrich) After mixing shrine Pori (ethylene glycol) (average-molecular-weight = 1500, average degree of polymerization = 33.7) to DMSO at a rate which serves as an equimolecular amount, respectively, mixture was dropped at 15 degrees C among inert gas into the 3 time mol equivalence of 2 and 4-JIISO cyanic-acid tolylene, and it flowed back at 80 degrees C.

[0040] Termination of a reaction was carried out until 2 and 4-JIISO cyanic-acid tolylene was no longer observed by gas chromatography.

[0041] The DMSO solution (1/the amount of 2 equivalent units) of PEI (30 \*\*\*\*\*) obtained by the same technique as an example 1 was dropped at the obtained DMSO solution in inert gas, and it flowed back at 130 degrees C, and reprecipitated like the example 1 after that, and the film cast of the obtained \*\*\*\* solution was carried out to the glass substrate, the vacuum drying was carried out at 140 degrees C one whole day and night, and the film excellent in the dimensional stability of independence nature was obtained.

[0042] The above-mentioned film was made to swell with the acetonitrile solution (for it to be 10.7 % of the weight to a film) of lithium perchlorate, the vacuum drying was again carried out for three days at 140 degrees C, propylene carbonate was added 19% of the weight to the solid polymer electrolyte as a plasticizer, and the solid polymer

electrolyte excellent in the dimensional stability of independence nature was obtained.

[0043] As a result of measuring the ionic conductivity of this thing like an example 1, it was  $3.2 \times 10^{-4}$  S/cm at the room temperature.

[0044]

[Example 3] In the example 2, various kinds of solid polymer electrolytes were similarly prepared except changing various additions of the lithium perchlorate to the prepared giant-molecule solid electrolyte.

[0045] The result of having measured ionic conductivity, such as this, is shown in the following table 2 with the added amount of lithium perchlorates.

[0046]

[Table 2]

塩濃度(重量%)	5. 9	10. 7	19. 2
イオン伝導率 (S/cm)	$9.8 \times 10^{-5}$	$3.2 \times 10^{-4}$	$7.3 \times 10^{-5}$

[0047] Table 2 also shows that this invention solid polymer electrolyte shows the outstanding ionic conductivity.

[0048]

[Example 4] The macromolecule base material of the chain length 20,000 [ about ] of a principal chain was obtained like the example 2.

[0049] Namely, Dow-Jones (Dow) Shrine 2-ethyl-2-oxazoline polymer (average molecular weight = 200,000) 10g was added into 300ml of concentrated hydrochloric acid, and the mixed solution of 200ml of distilled water, it hydrolyzed and principal chain polyethyleneimine was compounded.

[0050] Moreover, the reaction with the above-mentioned principal chain, a side chain, and a cross linking agent is a PEO derivative for side chains like an example 2. Aldrich (Aldrich) Shrine Pori (ethylene glycol methyl ether) (average-molecular-weight = 550, average degree of polymerization = 12.8) He is Aldrich (Aldrich) as a PEO derivative for cross linking agents. Shrine Pori (ethylene glycol) (average-molecular-weight = 1500, average degree of polymerization = 33.7) Side chain: It used by cross linking agent = 5:1 (mole ratio), this etc. was mixed with 2 and 4-JIISO cyanic-acid toylene (7 time mol equivalence of a cross linking agent), and it carried out by making mixture react with PEI (2 double mol equivalence of a cross linking agent) of a principal chain.

[0051] After drying the obtained macromolecule base material and considering as a heat (DMSO+PC (1:1)) solution, solvent exchange was carried out at the acetonitrile, after dissolving the lithium perchlorate which becomes 10.2 % of the weight to a macromolecule base material, after carrying out the film cast and removing a solvent to dry air at a room temperature one whole day and night, the vacuum drying was carried out at 130 more degrees C for 10 hours, and the desired solid polymer electrolyte was obtained.

[0052] It was  $3 \times 10^{-6}$  S/cm at the place and room temperature which measured the ionic conductivity of this thing.

[0053]

[Example 5] The side chain which makes the main frame the principal chain PEI of a degree of polymerization 30 and Pori (ethylene glycol methyl ether) of a mean molecular weight 550, and the macromolecule base material which consists of a cross linking agent which makes the main frame Pori (ethylene glycol) of a mean molecular weight 300 (average degree of polymerization = 6.4) were compounded like the example 2. The used diisocyanate is hexamethylene di-isocyanate and each preparation rate was set to principal chain:side-chain:cross linking agent:diisocyanate = 6:5:1:7 (mole ratio).

[0054] The acetonitrile was made to swell after drying the obtained macromolecule base material, the acetonitrile solution of the lithium perchlorate which becomes 5.4 % of the weight to a macromolecule base material was added, the solvent was distilled off, and the desired solid polymer electrolyte was obtained.

[0055] It was  $1 \times 10^{-7}$  S/cm at the place and room temperature which measured the ionic conductivity of this thing.

[0056]

[Example 6] The side chain which makes the main frame the principal chain PEI of a degree of polymerization 30 and Pori (ethylene glycol methyl ether) of a mean molecular weight 350 (average degree of polymerization 7.2), and the macromolecule base material which consists of a cross linking agent which makes the main frame Pori (ethylene glycol) of a mean molecular weight 1000 (average degree of polymerization = 22.3) were compounded like the example 2. The used diisocyanate is hexamethylene di-isocyanate and each preparation rate was set to principal

chain:side-chain:cross linking agent:diisocyanate =1:1:1:3 (mole ratio).

[0057] The acetonitrile was made to swell after drying the obtained macromolecule base material, the acetonitrile solution of the lithium perchlorate which becomes 9.6 % of the weight to a macromolecule base material was added, the solvent was distilled off, and the desired solid polymer electrolyte was obtained.

[0058] It was  $7 \times 10^{-6}$  S/cm at the place and room temperature which measured the ionic conductivity of this thing.

[0059]

[Example 7] He is Aldrich (Aldrich) like an example 2. The shrine Pori (ethyleneimine) (mean molecular weights 50,000-60,000) principal chain, the side chain which makes the main frame Pori (ethylene glycol methyl ether) of a mean molecular weight 350 (average degree of polymerization 7.2), and the macromolecule base material which consists of a cross linking agent which makes the main frame Pori (ethylene glycol) of a mean molecular weight 1000 (average degree of polymerization = 22.3) were compounded. The used diisocyanate is hexamethylene di-isocyanate and each preparation rate was set to principal chain:side-chain:cross linking agent:diisocyanate =1:1:1:3 (mole ratio).

[0060] The acetonitrile was made to swell after drying the obtained macromolecule base material, the acetonitrile solution of the lithium perchlorate which becomes 6.1 % of the weight to a macromolecule base material was added, the solvent was distilled off, and the desired solid polymer electrolyte was obtained.

[0061] It was  $2 \times 10^{-6}$  S/cm at the place and room temperature which measured the ionic conductivity of this thing.

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[Translation done.]

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PUBN-DATE: November 29, 1994

INVENTOR-INFORMATION:

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ASSIGNEE-INFORMATION:

NAME	COUNTRY
OSAKA GAS CO LTD	N/A

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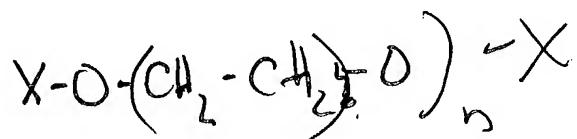
ABSTRACT:

PURPOSE: To obtain the title electrolyte comprising a polymer support and a supporting electrolyte and excellent in ionic conductivity, film-forming property, processability, flexibility, adherence to an electrode, etc., by using a specific polymer as the support.

CONSTITUTION: The polyelectrolyte comprises a polymer support and a supporting electrolyte, which is a crosslinked comb polymer obtained by crosslinking a comb polymer comprising a poly(ethylene imine), as the main chain, represented by the formula  
 $-(\text{NH}-\text{CH}[\text{SB}]2</\text{SB}>\text{CH}[\text{SB}]2</\text{SB}>)[\text{SB}]1</\text{SB}>$   
wherein 1 is 3 to 1&times;10 $^7$  and one or more side chains each bonded

to a nitrogen atom of the main chain and represented by the formula  
 $X-O-(CH<SB>2</SB>CH<SB>2</SB>O)<SB>m</SB>R<SB>1</SB>$  wherein X is  
a group  
represented by the formula  $O=C=N-R<SB>2</SB>-NH-CO$ -where R<SB>2</SB>  
is an  
arylene or alkylene; R<SB>1</SB> is a lower alkyl; and m is 3-100, the number  
of the side chains being at least 5% of the number of all nitrogen atoms of the  
main chain. The crosslinking is conducted with a crosslinking agent  
represented by the formula  
 $X-O-(CH<SB>2</SB>CH<SB>2</SB>O)<SB>n</SB>-X$  wherein  
n is 3-200 to such a degree that 1-95% of the nitrogen atoms of the main chain  
each has the crosslinked side chain.

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(54)【発明の名称】 含窒素高分子固体電解質

(57)【要約】

【構成】本発明は、高分子支持体と支持電解質とからなる高分子固体電解質において、高分子支持体が、特定のポリエチレンイミン主鎖と、ポリエチレンオキサイド系側鎖と、ポリエチレンオキサイド系架橋剤との3成分混合系樹型架橋高分子である含窒素高分子固体電解質を提供する。

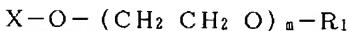
【効果】本発明含窒素高分子固体電解質は、高いイオン伝導率をもち、可撓性を有し、電池、コンデンサー、エレクトロクロミック表示素子、センサー等の電気化学素子のための優れた電解質として有効である。

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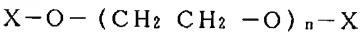
## 【特許請求の範囲】

【請求項1】高分子支持体と支持電解質とからなる高分子固体電解質において、高分子支持体が、式(1)－  
 $(\text{NH}-\text{CH}_2-\text{CH}_2)_1-$

〔式中1は3～ $1 \times 10^7$ の整数を示す〕で示されるポリエチレンイミン主鎖と、該主鎖のN位に置換する式(2)



〔式中Xは $\text{O}=\text{C}=\text{N}-\text{R}_2-\text{NH}-\text{CO}-$ ( $\text{R}_2$ はアリーレン鎖もしくはアルキレン鎖である)で示されるジイソシアネート片末端反応物を、 $\text{R}_1$ は低級アルキル基を、mは3～100の整数をそれぞれ示す〕で示されるポリエチレンオキサイド系側鎖とからなり、上記主鎖の窒素原子に対する側鎖の付加率が少なくとも5%である樹形高分子を、式(3)



〔式中Xは上記に同じであり、nは3～200の整数を示す〕で示されるポリエチレンオキサイド系架橋剤で架橋させて得られる、上記主鎖の窒素原子に対する側鎖の架橋率が1～95%の架橋樹形高分子であることを特徴とする含窒素高分子固体電解質。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は含窒素高分子固体電解質、より詳しくは電池、エレクトロクロミック表示素子、エレクトロルミネッセンス表示素子、コンデンサー、センサー等の電気化学素子等に有用な上記固体電解質に関する。

## 【0002】

【従来の技術】電池、エレクトロクロミックデバイス、コンデンサー等の電気化学素子は、電解液を使用しているため、液漏れによる信頼性の低下や、加工性、生産性等に問題があり、之等の問題を伴わない固体電解質の研究開発が、近年活発化してきている。該固体電解質の中でも高分子固体電解質は、無機系固体電解質に比べて、軽量で可撓性を有し、成形、加工性等に優れ、電極との密着性にも優れていることから、注目を集めている。

【0003】本発明者らも上記高分子電解質につき鋭意研究を重ねた結果、先に、主鎖に規則的な高次構造をとり高い極性を有するポリエチレンイミン(P.E.I.)を用い、側鎖に低分子のポリエチレンオキサイド(P.E.O.)をグラフトさせた高分子支持体の利用によれば、高いイオン伝導率を有すると共にフィルムキャストが可能な高分子固体電解質が得られることを見出だし、この知見に係わる発明を特許出願した(特開平4-270762号公報参照)。

【0004】しかしながら、上記先の出願に係わる高分子固体電解質は、更にイオン伝導率を向上させるために、適当な極性溶媒を可塑剤として混入させた場合や、70°C程度まで昇温した場合には、液状化し寸法安定性

が損なわれる欠点があった。

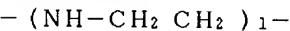
## 【0005】

【発明が解決しようとする課題】本発明の目的は、上記従来の高分子固体電解質、殊にこれに利用される高分子支持体に見られる欠点を悉く解消して、高いイオン伝導率、良好な成膜加工性、可撓性、電極との良好な密着性等を有する、斯界で要望される新しい高分子固体電解質を提供することにある。

## 【0006】

【課題を解決するための手段】本発明者は上記目的より更に引き続き研究を重ねた結果、高分子支持体として下記特定のポリエチレンイミン主鎖とポリエチレンオキサイド系側鎖とからなる樹形高分子を所定のポリエチレンオキサイド系架橋剤により架橋させた高分子を利用するときには、上記目的に合致する高分子固体電解質が得られることを見出だし、ここに本発明を完成するに至った。

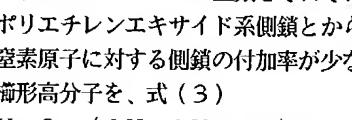
【0007】即ち、本発明によれば、高分子支持体と支持電解質とからなる高分子固体電解質において、高分子支持体が、式(1)



〔式中1は3～ $1 \times 10^7$ の整数を示す〕で示されるポリエチレンイミン主鎖と、該主鎖のN位に置換する式(2)



〔式中Xは $\text{O}=\text{C}=\text{N}-\text{R}_2-\text{NH}-\text{CO}-$ ( $\text{R}_2$ はアリーレン鎖もしくはアルキレン鎖である)で示されるジイソシアネート片末端反応物を、 $\text{R}_1$ は低級アルキル基を、mは3～100の整数をそれぞれ示す〕で示されるポリエチレンエキサイド系側鎖とからなり、上記主鎖の窒素原子に対する側鎖の付加率が少なくとも5%である樹形高分子を、式(3)



〔式中Xは上記に同じであり、nは3～200の整数を示す〕で示されるポリエチレンオキサイド系架橋剤で架橋させて得られる、上記主鎖の窒素原子に対する側鎖の架橋率が1～95%の架橋樹形高分子であることを特徴とする含窒素高分子固体電解質が提供される。

【0008】以下、本発明高分子固体電解質において利用される高分子支持体につき詳述すれば、該高分子支持体はこれを構成する主鎖として、前記式(1)で示されるポリエチレンイミン(P.E.I.)主鎖を用いる。その例としては例えば2-オキサゾリン類から合成されるポリエチレンイミン等が利用できる〔例えばMacromolecules Communications to Editor, 5, 108 (1972) 参照〕。該主鎖は一般に約15～50の鎖長(式(1)中の1)を有するのが好ましい。

【0009】本発明支持体は、上記P.E.I.主鎖と該主鎖のN位に置換する側鎖とから構成され、該側鎖は、極性解離基として機能するジイソシアノ酸誘導体を導入され

た前記式(2)で示されるポリエチレンオキサイド(PEO)の誘導体から構成される。該PEO系側鎖の導入は、例えば片末端が低級アルキル基( $R_1$ )で保護され、他方の片末端が水酸基であるPEO誘導体、例えばエチレングリコールモノメチルエーテルの3量体乃至100量体等を、ジメチルスルホキシド(DMSO)等のアプロティックな溶媒中で、2,4-ジイソシアニ酸トリレン等のジイソシアニ酸誘導体と、1:1モル等量で反応させることにより対応する前記式(2)で示されるPEO系誘導体を合成し、次いでこれを前記PEI主鎖に対応する直鎖状PEIと反応させることにより実施できる。ここで、低級アルキル基としては、例えばメチル、エチル、プロピル、イソプロピル、ブチル基等を例示できる。またジイソシアニ酸誘導体としては、 $R_2$ としてトリレン、キシレン、メタキシレン等のアリーレン鎖やヘキサメチレン、トリメチルヘキサメチレン、イソホロソ等の直鎖状乃至環状アルキレン鎖を有する各種の誘導体をいずれも利用できる。上記各反応の反応条件は特に限定されるものではないが、通常PEO系誘導体合成反応は、一般に室温~80°C程度の温度下、不活性ガス雰囲気中、アプロティックな溶媒中で原料を混合することにより実施され、側鎖の導入反応は、通常100~160°C程度の温度下、不活性ガス雰囲気中、アプロティックな溶媒中で原料を混合することにより実施され\*

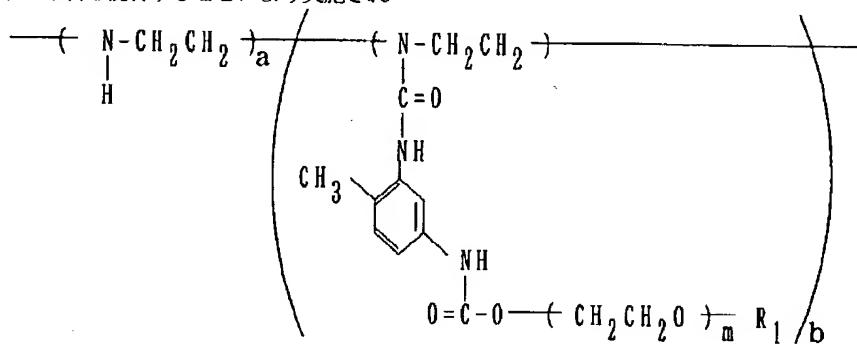
\*る。また、側鎖を導入するためのPEO系誘導体は、通常得られる高分子支持体の主鎖の単位ユニット100に対しても5~500程度となる割合で、直鎖状PEIに対して用いられるのが好ましく、かくして主鎖の窒素原子に対する側鎖の付加率が少なくとも5%である所望のPEI主鎖-PEO系側鎖高分子を収得できる。PEO系誘導体の使用割合が上記よりあまりに少なすぎると側鎖の導入率が低下し、得られる高分子のイオン伝導率が低下する欠点がある。逆に上記500を上回る場合は未反応物が多くなり過ぎその除去に繁雑な操作を要する不利がある。

【0010】尚、上記式(2)で示されるPEO系誘導体の如き低分子量物は、それ単独では液体であるが、本発明支持体中ではこれが側鎖として存在するため、寸法安定性に優れ、またイオンの伝導に大きく寄与するPEO鎖のミクロブラウン運動が活発に行なわれることが期待できる。

【0011】かくして得られるPEI主鎖-PEO系側鎖高分子は、例えば2,4-ジイソシアニ酸トリレンを用いた場合を例にとれば、下記式(4)で示される如き樹形構造を有している。

【0012】

【化1】



【0013】式中 $R_1$ 及び $m$ は前記に同じ、 $a+b=1$ であり、 $95>100b/a+b>5$ を示す。

【0014】本発明支持体は、上記PEI主鎖-PEO系側鎖樹形高分子を、前記式(3)で示されるポリエチレンオキサイド(PEO)系架橋剤を用いて架橋反応させることにより製造される。該PEO系架橋剤は、例えば両末端が水酸基であるPEO( $n=3\sim 200$ )を、DMSO等のアプロティックな溶媒中で、2,4-ジイソシアニ酸トリレン等のジイソシアニ酸誘導体の2倍モル等量と反応させることにより得られる。この反応は、前記PEO系誘導体合成反応と略同様の反応条件下に実施できる。また該架橋剤を用いたPEI主鎖-PEO系側鎖樹形高分子の架橋反応は、前記側鎖の導入反応と略同様の反応条件下にて実施でき、PEO系架橋剤の添加量は、架橋率が5~60%程度となるように選択される※50

※のが好ましい。ここで架橋率とは、主鎖の窒素原子に対する架橋剤の使用モル比(百分率)で示される。該架橋率が上記範囲を満たさない場合、即ちPEI主鎖-PEO系側鎖高分子に対するPEO系架橋剤の使用割合があまりに少なすぎる場合は、得られる高分子の機械的強度や寸法安定性が低下する傾向があり、逆に架橋剤の使用割合があまりに多すぎる場合は、高分子のイオン伝導率が低下する傾向にあり、いずれも好ましくない。

【0015】かくして上記PEO系架橋剤を利用した架橋反応によって、前記PEI主鎖-PEO系側鎖樹形高分子のPEI主鎖に存在する未反応NH基に、該架橋剤が反応して、所望の架橋樹形高分子支持体が形成される。

【0016】上記高分子支持体は、これに常法に従い支持電解質を含浸させることにより、高いイオン伝導率、

高温や可塑剤の添加によっても優れた成膜性を有する所望の自立性含窒素高分子固体電解質とすることができる。

【0017】ここで用いられる支持電解質は、特に制限されるものではなく、公知の各種のもののいずれでもよい。その具体例としては、例えばp-トルエンスルホン酸、酢酸、蔥酸、ポリビニルスルホン酸、トリフルオロメタンスルホン酸、トリフルオロ酢酸、等の有機酸、リン酸、過塩素酸、チオシアン酸、テトラクロロホウ酸、ヘキサフルオロリン酸、トリフルオロ酢酸、硝酸等の無機酸等の各種酸類や之等各種酸と、例えばハロゲン、アルカリ金属、アルカリ土類金属、テトラブチルアンモニウムやテトラエチルアンモニウム等の4級アンモニウム等との反応による各種の塩類を例示できる。之等支持電解質の含浸も通常の方法に従い行なうことができる。より具体的には、例えばアセトニトリル、クロロホルム、メタノール、N,N-ジメチルホルムアミド、ジメチルスルホキシド、プロピレンカーポネット、エチレンカーポネット、ジエチルカーポネット等の溶媒や之等の混合溶媒に、前記高分子支持体と支持電解質とを溶解させ、得られる溶液をフィルムキャストする方法、前記高分子支持体と支持電解質とを無溶媒で均一に混合し、高分子支持体が軟化する温度で支持電解質を溶解させる方法等を例示できる。

【0018】かくして得られる本発明含窒素高分子固体電解質は、通常約 $1 \times 10^{-3} \sim 1 \times 10^{-8}$  S/cm程度の高いイオン伝導率( $\sigma$ )を示す。

#### 【0019】

【発明の効果】本発明含窒素高分子固体電解質は、通常約 $1 \times 10^{-3} \sim 1 \times 10^{-8}$  S/cm程度の高いイオン伝導率( $\sigma$ )をもち、可撓性を有し、電池、コンデンサー、エレクトロクロミック表示素子、センサー等の電気化学素子のための優れた電解質として有効である。特に、本発明の固体電解質は常温でのイオン伝導率が非常に高く、充放電特性の優れた電池やコンデンサー、応答速度の早いエレクトロクロミック表示素子、発光効率の高いエレクトロルミネッセンス表示素子やセンサー等の製造に非常に有効である。

#### 【0020】

【実施例】以下、本発明を更に詳しく説明するため、実施例及び比較例を挙げる。

#### 【0021】

【実施例1】アルドリッヂ(Aldrich)社製2-メチル-2-オキサゾリンのリビング重合体を、以下の通り加水分解してPEI主鎖を合成した〔Macromolecules, 8, 390 (1975) 参照〕。2-メチル-2-オキサゾリンのリビング重合開始剤としてp-トルエンスルホン酸メチルを用い、仕込みモル比は1/30とした。反応は、アセトニトリルを溶媒として不活性ガス雰囲気中で還流し、反応の終了はガスクロマトグラフィーにより決定した。

【0022】かくして得られた30量体のポリ(N-アセチルイミン)を、約100g/1等量の水溶液とし、更にこれに約900g/1等量のNaOHを加え、一昼夜還流して、主鎖に対応する直鎖状ポリエチレンイミン(PEI、30量体)を得た。

【0023】側鎖に対応するPEO誘導体として、アルドリッヂ(Aldrich)社製ポリ(エチレングリコールメチルエーテル)(平均分子量=550、平均重合度=12.8)を用いた。

10 【0024】上記PEIへのPEO誘導体の付加を、2,4-ジイソシアントリレンを用いて以下の通り行なった。即ち、ジメチルスルホキシド溶媒中、2,4-ジイソシアントリレンに不活性ガス中でポリ(エチレングリコールメチルエーテル)を1:1のモル比で混合し、室温で一昼夜搅拌して、まず前記式(2)に対応する側鎖を形成し得るPEO系誘導体を合成した。

【0025】得られた反応混合溶液から未反応の2,4-ジイソシアントリレンを取り除くために減圧蒸留を行ない、次いでこれにジメチルスルホキシド及び上記で合成したPEI(等量ユニット量)を順次加え、一昼夜搅拌してPEI主鎖-PEO系側鎖からなる樹形高分子を含むジメチルスルホキシド溶液を得た。

20 【0026】上記で得られた高分子の側鎖の付加率は元素分析の結果から6.4%と判明した。

【0027】PEO系架橋剤として、アルドリッヂ(Aldrich)社製ポリ(エチレングリコール)(平均分子量=1500、平均重合度=33.7)を用いた。

30 【0028】上記PEO系架橋剤を前記樹形高分子に付加させた。即ち、ジメチルスルホキシド溶媒中、2,4-ジイソシアントリレンに不活性ガス中でポリ(エチレングリコール)を1/2モル等量混合し、室温で一昼夜搅拌して、前記式(3)で示される架橋剤を得た。

【0029】得られた反応混合溶液から未反応の2,4-ジイソシアントリレンを取り除くために減圧蒸留を行ない、次いでこれにジメチルスルホキシド及び上記で合成した樹形高分子を順次加え、一昼夜還流して、目的の架橋樹形高分子を含むジメチルスルホキシド溶液を得た。

40 【0030】得られた溶液を減圧蒸留して、反応混合物からジメチルスルホキシドを取り除き、その後残留物をアセトニトリルに溶解し、ジエチルエーテルで再沈殿させた後、同様にして、メタノール、ベンゼン溶液をジエチルエーテルで再沈殿させて、目的の高分子支持体を分離精製した。

【0031】得られた高分子支持体の架橋率は、元素分析結果より、28%と判明した。

【0032】この高分子支持体を乾燥し、熱(DMSO+PC(1:1))溶液にした後、アセトニトリルに溶媒交換を行ない、高分子支持体に対して10.2重量%となる過塩素酸リチウムを溶解後、フィルムキャスト

し、一昼夜室温で乾燥し、空気で溶媒を取り除いた後、更に10時間、130°Cで真空乾燥して、高分子固体電解質を調製した。

【0033】得られた高分子固体電解質の物性としてガラス転移温度とイオン伝導率( $\sigma$ )を測定した。

【0034】セイコー電子工業株式会社製DSC220Cにより測定したガラス転移温度は、-48.7°Cであった。

\* 【0035】ソーラートロン(Solartron)社製1260 IMPEDANCE/GAIN-PHASE ANALYZERにより、1Hz~10MHzの範囲で交流インピーダンスを測定し、Cole-ColePlotを得ることにより評価したイオン伝導率( $\sigma$ )の温度依存性は、下記表1に示す通りであった。

【0036】

【表1】

\*

温 度 (°C)	$1000/T$ ( $10^{-3} \cdot K^{-1}$ )	$\sigma$ ( $S/cm$ )	Log [ $\sigma$ ( $S/cm$ )]
86.0	2.78	$2.0 \times 10^{-3}$	-2.7
78.4	2.84	$1.6 \times 10^{-3}$	-2.8
72.7	2.89	$1.4 \times 10^{-3}$	-2.8
66.3	2.95	$1.2 \times 10^{-3}$	-2.9
61.2	2.99	$1.1 \times 10^{-3}$	-3.0
51.9	3.08	$7.6 \times 10^{-4}$	-3.1
46.0	3.13	$6.2 \times 10^{-4}$	-3.2
39.2	3.20	$4.5 \times 10^{-4}$	-3.3
35.0	3.25	$3.8 \times 10^{-4}$	-3.4
30.2	3.30	$3.0 \times 10^{-4}$	-3.5
25.8	3.35	$2.4 \times 10^{-4}$	-3.6
21.9	3.39	$1.9 \times 10^{-4}$	-3.7
15.8	3.46	$1.4 \times 10^{-4}$	-3.9
-0.3	3.67	$4.0 \times 10^{-5}$	-4.4
-2.9	3.70	$3.2 \times 10^{-5}$	-4.5
-8.2	3.77	$1.8 \times 10^{-5}$	-4.7

【0037】該表より、本発明高分子固体電解質フィルムは、室温で $2 \times 10^{-4} S/cm$ という高いイオン伝導率を示し、更にその温度依存性も低く、例えば-8°Cでも $2 \times 10^{-5} S/cm$ という優れた特性を示すことが明らかである。

【0038】

【実施例2】実施例1では、側鎖、架橋剤を順次添加反応させることにより、本発明高分子固体電解質のための架橋樹形高分子支持体を調製したが、本例では両者を混合状態で添加反応させて所望の高分子固体電解質のための支持体を調製した。

【0039】即ち、側鎖用PEO誘導体としてアルドリッヂ(Aldrich)社製ポリ(エチレングリコール)(平均分子量=40

※-テル)(平均分子量=550、平均重合度=12.8)を、架橋剤用PEO誘導体としてアルドリッヂ(Aldrich)社製ポリ(エチレングリコール)(平均分子量=1500、平均重合度=33.7)を、それぞれ等モル量となる割合でDMSOに混合した後、混合物を2,4-ジイソシアントリレンの3倍モル等量中に、不活性ガス中、15°Cで滴下し、80°Cで還流した。

【0040】反応の終了はガスクロマトグラフィーにより2,4-ジイソシアントリレンが観測されなくなるまでとした。

【0041】得られたDMSO溶液に、実施例1と同様の手法により得られたPEI(30量体)のDMSO溶液(1/2等量ユニット量)を、不活性ガス中で滴下

し、130°Cで還流し、以後実施例1と同様にして再沈殿を行ない、得られた粘張溶液をガラス基板にフィルムキャストし、140°Cで一昼夜真空乾燥して、自立性の寸法安定性に優れたフィルムを得た。

【0042】上記フィルムを、過塩素酸リチウムのアセトニトリル溶液（フィルムに対し10.7重量%）で膨潤させ、再度140°Cで3日間真空乾燥し、可塑剤としてプロピレンカーボネートを高分子固体電解質に対して19重量%添加して、自立性の寸法安定性に優れた高分子固体電解質を得た。

【0043】このもののイオン伝導率を実施例1と同様\*

塩濃度(重量%)	5.9	10.7	19.2
イオン伝導率 (S/cm)	$9.8 \times 10^{-5}$	$3.2 \times 10^{-4}$	$7.3 \times 10^{-5}$

【0047】表2からも、本発明高分子固体電解質は優れたイオン伝導率を示すことが判る。

【0048】

【実施例4】実施例2と同様にして、主鎖の鎖長約2万の高分子支持体を得た。

【0049】即ち、ダウ(Dow)社製2-エチル-2-オキサゾリンポリマー（平均分子量=20万）10gを濃塩酸300ml及び蒸留水200mlの混合溶液中に加え、加水分解して主鎖ポリエチレンイミンを合成した。

【0050】また上記主鎖と側鎖及び架橋剤との反応は、実施例2と同様にして、側鎖用PEO誘導体としてアルドリッヂ(Aldrich)社製ポリ(エチレングリコールメチルエーテル)（平均分子量=550、平均重合度=12.8）を、架橋剤用PEO誘導体としてアルドリッヂ(Aldrich)社製ポリ(エチレングリコール)（平均分子量=1500、平均重合度=33.7）を、側鎖：架橋剤=5:1(モル比)で用い、之等を2,4-ジイソシアノ酸トリレン（架橋剤の7倍モル等量）と混合し、混合物を主鎖のPEI（架橋剤の2倍モル等量）と反応させることにより行なった。

【0051】得られた高分子支持体を乾燥し、熱(DM SO+PC(1:1))溶液とした後、アセトニトリルに溶媒交換し、高分子支持体に対して10.2重量%となる過塩素酸リチウムを溶解後、フィルムキャストし、一昼夜室温で乾燥空気に溶媒を取り除いた後、更に130°Cで10時間真空乾燥して、所望の高分子固体電解質を得た。

【0052】このもののイオン伝導率を測定した所、室温で $3 \times 10^{-6} \text{ S/cm}$ であった。

【0053】

【実施例5】実施例2と同様にして、重合度30の主鎖※50

\*にして測定した結果、室温で $3.2 \times 10^{-4} \text{ S/cm}$ であった。

【0044】

【実施例3】実施例2において、調製した高分子固体電解質に対する過塩素酸リチウムの添加量を種々変化させる以外は同様にして、各種の高分子固体電解質を調製した。

【0045】之等のイオン伝導率を測定した結果を、添加した過塩素酸リチウム量と共に、下記表2に示す。

10 【0046】

【表2】

20 ※PEI、平均分子量550のポリ(エチレングリコールメチルエーテル)を主骨格とする側鎖、平均分子量300(平均重合度=6.4)のポリ(エチレングリコール)を主骨格とする架橋剤からなる高分子支持体を合成した。用いたジイソシアネート類はヘキサメチレンジイソシアネートであり、それぞれの仕込み割合は、主鎖：側鎖：架橋剤：ジイソシアネート類=6:5:1:7(モル比)とした。

【0054】得られた高分子支持体を乾燥後、アセトニトリルに膨潤させ、高分子支持体に対して5.4重量%となる過塩素酸リチウムのアセトニトリル溶液を加え、溶媒を留去して、所望の高分子固体電解質を得た。

30 【0055】このもののイオン伝導率を測定した所、室温で $1 \times 10^{-7} \text{ S/cm}$ であった。

【0056】

【実施例6】実施例2と同様にして、重合度30の主鎖PEI、平均分子量350(平均重合度7.2)のポリ(エチレングリコールメチルエーテル)を主骨格とする側鎖、平均分子量1000(平均重合度=22.3)のポリ(エチレングリコール)を主骨格とする架橋剤からなる高分子支持体を合成した。用いたジイソシアネート類はヘキサメチレンジイソシアネートであり、それぞれの仕込み割合は、主鎖：側鎖：架橋剤：ジイソシアネート類=1:1:1:3(モル比)とした。

40 【0057】得られた高分子支持体を乾燥後、アセトニトリルに膨潤させ、高分子支持体に対して9.6重量%となる過塩素酸リチウムのアセトニトリル溶液を加え、溶媒を留去して、所望の高分子固体電解質を得た。

【0058】このもののイオン伝導率を測定した所、室温で $7 \times 10^{-6} \text{ S/cm}$ であった。

【0059】

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【実施例7】実施例2と同様にして、アルドリッチ(Aldrich)社製のポリ(エチレンイミン)(平均分子量5万～6万)主鎖、平均分子量350(平均重合度7.2)のポリ(エチレングリコールメチルエーテル)を主骨格とする側鎖、平均分子量1000(平均重合度=22.3)のポリ(エチレングリコール)を主骨格とする架橋剤からなる高分子支持体を合成した。用いたジイソシアネート類はヘキサメチレンジイソシアネートであり、そ

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れぞれの仕込み割合は、主鎖：側鎖：架橋剤：ジイソシアネート類=1:1:1:3(モル比)とした。

【0060】得られた高分子支持体を乾燥後、アセトニトリルに膨潤させ、高分子支持体に対して6.1重量%となる過塩素酸リチウムのアセトニトリル溶液を加え、溶媒を留去して、所望の高分子固体電解質を得た。

【0061】このもののイオン伝導率を測定した所、室温で $2 \times 10^{-6} \text{ S/cm}$ であった。